and $\theta = d/r$, where d is the diameter of the lens;

hence $\theta = d/b . 2 \sin\frac{1}{2}\Theta.$

The other columns of the table explain themselves.

On the whole, I think it must be concluded that Insects do not see well, at any rate as regards their power of defining distant objects, and their behaviour certainly favours this view; but they have an advantage over simple-eyed animals in the fact that there is hardly any practical limit to the nearness of the objects they can examine. With the composite eye, indeed, the closer the object the better the sight, for the greater will be the number of lenses employed to produce the impression; whereas in the simple eye the focal length of the lens limits the distance at which a distinct view can be obtained.

The best of the eyes mentioned in the table would give a picture about as good as if executed in rather coarse wool-work and viewed at a distance of a foot; and, although a distant landscape could only be indifferently represented on such a coarse-grained structure, it would do very well for things near enough to occupy a considerable part of the field of view.

II. "The Action of Heat upon Ethylene." By VIVIAN B. LEWES. Professor of Chemistry in the Royal Naval College, Greenwich. Communicated by Professor THORPE, F.R.S. Received December 6, 1893.

The decompositions of the simpler forms of hydrocarbons at an elevated temperature have always been recognised as a question of the greatest importance, as upon them is dependent a true conception of many of the actions taking place in the manufacture of coal gas and other kindred processes of destructive distillation.

Ethylene has in most cases been chosen as the hydrocarbon which would lend itself most readily to experimental researches upon this point, as, besides being one of the simplest, it is easily prepared, and is moreover found as one of the products in nearly all cases where organic compounds are subjected to distillation at high temperatures.

No sooner had the difference between ethylene and methane been recognised, than experiments were made by Deimann, Van Troostwyk, Lauwerenburg, and Bondt* to ascertain the action of heat upon the newly-formed compound, and the conclusions which they came to were that on heating no contraction in volume was observed, but that the tubes in which the decomposition was effected became coated with a black deposit, and drops of an oily body were formed, the gas

* 'Annales de Chimie et de Physique,' 1st series, vol. 21, p. 48.

at the same time losing its property of forming an oily liquid with chlorine.

These experiments were afterwards repeated by Fourcroy, Hecht, and Vauquelin,* who showed that when heated, ethylene yields hydrogen with deposition of carbon, whilst in 1805 William Henry† showed that ethylene was formed during the destructive distillation of organic bodies, and that on further heating the gas, other changes were observed, and the gas was eventually converted into carbon and hydrogen. The deposition of carbon was also noticed later by Quet,‡ who on passing sparks through ethylene found that carbon was deposited, and formed a bridge between the poles used for the discharge, whilst Dalton showed by the continuous action of the electric spark that ethylene yielded double its own volume of hydrogen, carbon being deposited.

Marchand§ came to the conclusion that at a red heat this gas splits up into methane and carbon, but at a white heat into carbon and nearly pure hydrogen, whilst Magnus, in 1847, made the important observation that on leading ethylene through a red-hot tube a contraction in volume followed ; the residual gas consisted of methane, hydrogen, and unchanged ethylene, whilst carbon was deposited, and fluid and even solid hydrocarbons were obtained.

In 1860 H. Buff and A. W. Hofmann‖ published a paper on the " Dissociation of Gaseous Compounds on Heating by Electricity."

They found that when a platinum spiral is heated by the galvanic current in pure ethylene there is at once a visible separation of carbon, which covers the sides of the tubes with a black deposit, whilst hardly any expansion in the volume of the gas takes place, from which they assume that the ethylene has split up into methane and carbon.

If the action on the gas, due to the incandescent platinum wire, is allowed to continue, then an increased amount of the gas undergoes dissociation, and soon after the separation of carbon commenced, they observed an expansion which is rapid at first, and in ten minutes reaches a maximum. Similar phenomena were noticed with the spark current; at first the spark had a pale reddish tint which gradually turned to violet, immediate separation of carbon taking place, the spark being frequently stopped by scales of carbon which formed a bridge between the poles. They found that under these conditions the volume of gas expands very rapidly at first but afterwards more slowly, and that after twenty to twenty-five minutes, the point of maxi-

---

* Gilbert's ' Annalen,' vol. 2, p. 210.

† ' Nicholson's Journal,' 1805.

‡ ' Comptes Rendus,' vol. 42, p. 903.

§ ' J. für prakt. Chem.,' vol. 26, p. 478.

‖ Liebig's ' Annalen der Chemie,' vol. 113, p. 119.

mum expansion is reached, so that 7 c.c. of dry ethylene gave, after decomposition, 12·25 c.c.   They noted also that the residual hydrogen had an unpleasant smell, and burnt with a slightly luminous flame.

Berthelot,[*] in 1869, claims that ethylene breaks up under the influence of heat into acetylene and hydrogen, as expressed by the equation

$$C_2H_4 = C_2H_2 + H_2,$$
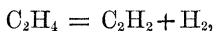
and shows that the acetylene then polymerises into benzene, styrene, and other liquid products of higher boiling points.   Naphthalene was also formed by the direct condensation of styrene and acetylene.   He also points out that during the heating of ethylene a large proportion of ethane was formed, and his final conclusion is that the heating of ethylene results in the splitting up of 2 mols. of ethylene into acetylene and ethane, and that the formation of solid and liquid products is due to the subsequent condensation of the acetylene.

In 1886[†] Day made a number of experiments in order to determine the lowest point of temperature at which the constitution of ethylene undergoes alteration, and the nature of the changes taking place at that temperature.   In order to do this, he devised an ingenious apparatus in which the ethylene could be heated for very long periods in a hard-glass tube.   From these experiments he concluded that when the action is continued over a long period the gas undergoes change at much lower temperatures than had been previously observed.   The alteration in constitution commences at about 350° C., at which temperature the change is one of condensation without the formation of members of any series of hydrocarbons having a percentage of hydrogen and carbon different from ethylene, whilst if ethylene is maintained at 400° for a sufficient length of time, it is entirely decomposed, marsh gas, ethane, and liquid products being obtained.

In the same year Messrs. Morton and Noyes[‡] made an elaborate investigation with the object of determining whether crotonylene, C_4H_4, which is present in small quantities in illuminating gas and other products of the distillation of organic matter, is formed as a primary product of decomposition by heat, or as a secondary product of the action of heat upon ethylene.

Coal gas was passed slowly through a hard glass tube 15 mm. in diameter, which was maintained at a low red heat for a distance of 60 cm.   The products issuing from this tube were first passed through a series of ∪-tubes surrounded by a freezing mixture; the products which were not condensed were passed through an ammoniacal solution of cuprous chloride, to absorb hydrocarbons of the

    * ' Annales de Chimie et de Physique,' 4th series, vol. 16, p. 144.
   † ' American Chemical Journal,' vol. 8, p. 153.
    ‡ *Ibid.*, vol. 8, p. 362.

acetylene series, whilst samples of the gases escaping absorption were finally collected over water. Carbon was deposited in the decomposition tube, and at the end of one month 15 c.c. of liquid had been slowly condensed in the ∪-tubes, and in this liquid they detected benzene, naphthalene, anthracene,' and some other aromatic hydrocarbons, present in quantities too small for determination. Faint traces only of precipitate were found in the ammoniacal cuprous chloride solution, whilst among the bodies absorbed by bromine they identified crotonylene tetrabromide, and the gas collected over water proved to be a mixture of methane and ethane. The absence of acetylene from the products obtained led them to the view that these products are formed directly by the action of heat upon ethylene.

From the work of the earlier observers, the text-books have accepted the equation

$$1. \quad C_2H_4 = C_2 + 2H_2$$
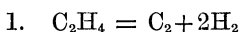
as representing the decomposition which takes place at a very high temperature, whilst, on the evidence of the work done by Marchand, and Buff and Hofmann, they represent the change taking place at a lower temperature by the equation

$$2. \quad C_2H_4 = C + CH_4.$$
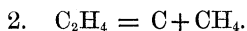
During my attempts to trace the actions taking place in the inner zone of luminous flames, I was struck by the complexity of the changes, and the absence of any evidence which would tend to confirm the second equation, and I have made the experiments detailed in the following paper in the hope of being able to trace the decomposition effected by heat in such simple hydrocarbons as ethylene, ethane, and methane.

The first step was to make experiments to corroborate the statement made by Day that, if ethylene is heated at 400° C. for a sufficient length of time, it is entirely decomposed, with formation of methane, ethane, and liquid products.

In order to do this an apparatus of the form used by Day in his experiments was employed, the only difference being that instead of using an air thermometer, the temperature was taken by means of a platinum and platinum-rhodium couple—as introduced by Le Châtelier, and fully described by Mr. C. Roberts-Austen—which had been previously carefully calibrated, employing salts of known fusing points. The ethylene was prepared for this and for all the following experiments by making a mixture of 25 parts by weight of rectified methylated spirit and 150 parts of strong sulphuric acid. The mixture was heated in a flask containing a layer of sand, and the gas evolved was washed by contact with strong sulphuric acid, and by passage through several bottles containing a strong solution of caustic soda. The gas was stored in a glass gas-holder for several days over water

containing sodic pyrogallate and sodic hydrate, to absorb all traces of oxygen, and on analysis gave

$$\begin{array}{ll} \text{Ethylene.......... } & 98\cdot 80 \\ \text{Nitrogen.......... } & 1\cdot 20 \end{array}$$

The gas was then passed through the combustion tube, until it was considered that all air had been displaced, and the tube was maintained for 100 hours at 400° C. Oil and a very small quantity of carbon deposited in the tube, and the volume decreased from 100 to 61. The gas was then removed from the tube and analysed.

In all the analyses described in this paper the following procedure was adopted. Carbon dioxide was absorbed by means of a 50 per cent. solution of sodic hydrate, the oxygen estimated by absorption with alkaline pyrogallate, the unsaturated hydrocarbons next absorbed by means of a solution of bromine in potassium bromide, care being taken to remove bromine vapour from the gas by agitation with caustic soda before measurement, the carbon monoxide was next estimated by acid cuprous chloride, and after removal of any acid fumes the residual gas was treated with paraffin oil, previously prepared for use by heating it over a water-bath for at least an hour.

Experiments show that in the case of mixtures of methane with higher members of the same group, agitation with paraffin prepared in this way, or mere standing in contact with it with occasional agitation for twenty to thirty minutes, will remove the ethane and any higher saturated hydrocarbons which may be present, together with a small proportion of the methane. The amount of residual methane can then be determined by explosion with oxygen, and subsequent estimation of the carbon dioxide formed, the volume of gas absorbed by the paraffin *plus* the volume resulting from explosion giving the total volume of saturated hydrocarbons. Details of the results obtained by this method of procedure when dealing with gaseous mixtures of known composition will be found, 'Jour. Soc. Chem. Industry,' vol. 10, p. 407.

The analysis of the heated ethylene gave

$$\begin{array}{lr} \text{Carbon dioxide......................... } & 0\cdot 82 \\ \text{Oxygen .... } & 0\cdot 00 \\ \text{Unsaturated hydrocarbons.............. } & 7\cdot 00 \\ \text{Carbon monoxide...................... } & 1\cdot 17 \\ \text{Saturated hydrocarbons—Paraffin.. } \quad 40\cdot 18 \Big\} \ 61\cdot 82 \\ \qquad\qquad\qquad\qquad \text{Explosion} \quad 21\cdot 64 \\ \text{Hydrogen............................. } & 22\cdot 18 \\ \text{Nitrogen............................. } & 7\cdot 01 \end{array}$$

$$\overline{\hspace{2cm} 100\cdot 00}$$

the oxides of carbon and increase on the nitrogen showing that some air had remained in the tube.

A second analysis was now made, but instead of estimating the saturated hydrocarbons by first absorbing the higher members and some methane by paraffin, they were exploded with oxygen, and the methane calculated from the carbon dioxide amounted to 112·5 per cent., showing that ethane and probably even higher members of the series were present, results which fully bear out the statement made by Day as to the decomposition of the ethylene taking place at a temperature of 400° C., and also the statements made by Berthelot and by Day, that under the conditions of this experiment ethane or at any rate higher members of the C_nH_{2n+2} series are formed as well as methane.

It would, however, be manifestly wrong to assume that the formation of the higher paraffins was a primary action, as keeping the hydrocarbons formed by the primary changes at a temperature of 400° C. might easily lead to the formation of secondary products by interaction between the gases.

It seemed much more probable that the character of the primary decompositions would be ascertained by rapidly heating the gas, and as rapidly removing the products of decomposition from the influence of heat, and that this would be effected by passing a regular current of the gas through a very narrow tube heated for 140 mm. to a known temperature.

The necessity for heating this tube to temperatures above 1000° C. practically limited the choice of material of which it could be made to fire-clay or platinum. It was at first feared that the use of the latter might interfere with the changes taking place, but a long series of comparative experiments, in which ethylene was decomposed by passing through (*a*) a pipe-stem glazed with borax, and (*b*) a platinum tube 2 mm. in diameter, both being heated to the same temperature, showed that the platinum tube was free from experimental objection unless a considerable percentage of oxygen was present, and that, even with a new tube, the decompositions were of the same nature as when the pipe-stem was employed.

Under these conditions the platinum tube possessed so many advantages over the clay pipe that in all the subsequent experiments a platinum tube, 2 mm. in diameter and about 40 cm. in length, was used, and, in order to accurately measure the temperature to which the gas in the tube was heated, the following arrangement was devised :—

Ethylene was stored in a gas-holder, and, after passing over calcic chloride to dry it, entered the platinum tube. In this tube the platinum and the platinum-rhodium thermo-couple was arranged in the following fashion :—

The two wires are twisted together for a length of 3 mm., and the wires on either side of the twist are then passed through thin glass tubes, which are fused on to them; having been in this way coated with glass so that only the twist is exposed, they are passed through the platinum tube, the glass insulating the wire from the tube, and also keeping the thermo-junction in such a position that it registers the temperature of the gas in the tube, not that of the wall of the tube.

To each end of the platinum tube glass ⊤-pieces are fitted, down the stems of which the wires pass to mercury seals; from the metal seals conducting wires lead to the resistance coils, the key, and a reflecting galvanometer. The products, after leaving the platinum tube, pass through a ⋃-tube, cooled in ice and salt in order to condense any liquids, and then through a collecting tube, from which the sample of gas for analysis for gas is taken, thence to Volhard absorption flasks (containing ammoniacal silver nitrate for the estimation of acetylene), the flow of the gas through the apparatus being regulated by means of the aspirator bottle.

In the following set of experiments the ethylene, after purification from oxygen by standing over a dilute solution of sodic pyrogallate and sodic hydrate, was passed through the tube at the rate of about 10 c.c. per minute.

These experiments are of considerable interest, as they throw some light upon the changes taking place during the heating of ethylene.

The gas being passed through 140 mm. of heated tube, no change takes place until a temperature of 800° C. is reached, when traces of acetylene are observed; between 800° and 900° C. the acetylene increases in quantity, and large quantities of methane are generated, accompanied by liquid products. This action increases until just below 1200° C., when hydrogen begins to appear amongst the products of decomposition, whilst the moment the liberation of hydrogen commences, carbon also is deposited; and the formation of oil decreases until close upon 1500° C., when the decomposition of the ethylene is practically complete, and the products of decomposition are mainly hydrogen with some undecomposed methane, and a copious deposit of carbon.

In each experiment the products of decomposition were examined to see if any member of the C_nH_{2n+2} group other than methane was present, and in no case could any be detected. This seems to point strongly to the conclusion that the ethane formed in the previous experiment, in accordance with the experiments of Day and Berthelot, had its origin as a secondary, and not as a primary, product of decomposition, but it was clear that to determine this point other experiments must be made, to see if under these conditions of tem-

Table I.—The Action of Heat upon flowing Ethylene.

Percentage of ethylene in original gas.	96·78	96·78	96·78	94·8	94·8	98·91	98·91
Temperature of gas in decomposing tube	600° C.	700° C.	800° C.	900° C.	1000° C.	1200° C.	1500° C.

Analysis of gas after heating, per cent.

Unsaturated hydrocarbons........	96·42	96·39	96·46	34·77	18·02	10·54	0·43
Containing acetylene..	0·00	0·00	trace	0·82	0·60	3·60	0·00
Saturated hydrocarbons .	0·00	0·00	0·00	59·73	76·48	55·26	27·80
Hydrogen....	0·00	0·00	0·00	0·00	0·00	25·11	62·68

Carbon deposited and oil formed in grams per 100 c.c.

Carbon......	0·00	0·00	0·00	0·00	0·00	0·0273	large quantity
Oil	0·00	0·00	0·00	0·0024	0·0048	0·0038	0·00
Change of volume	none	none	none	decrease	decrease	increase	large increase

perature a slower rate of flow was attended by generation of any saturated hydrocarbons higher than methane.

In order to do this, the same arrangement of apparatus was employed, but the rate of flow of ethylene was diminished to 4·2 c.c. per minute, the gas, after heating, being collected as before, and an analysis made in which the saturated hydrocarbons were calculated from the results of the paraffin absorption and subsequent explosion. A second analysis was then made of the heated gas without any paraffin absorption, and the volume of carbon dioxide formed on explosion calculated as methane. If the volume so obtained is found to be greater than that originally given by the combined paraffin absorption and subsequent explosion, it is held to be evidence that some higher member of the paraffin series must be present. In order to ascertain if any unsaturated hydrocarbon other than ethylene is present in the gas after heating, a sample of the gas is exploded with oxygen, and the carbon dioxide estimated; should the amount formed exceed the carbon dioxide calculated from the second analysis, it may be taken as evidence that an unsaturated hydrocarbon higher than ethylene is present.

Analysis of the Ethylene used in these experiments.

Carbon dioxide	Nil
Oxygen	0·24
Ethylene	98·55
Nitrogen	1·21
Methane	Nil
Hydrogen	Nil
	100·00

Table II.—The Action of Heat upon Ethylene flowing at the rate of 4·2 c.c. per minute through 6 in. of heated tube.

I. Analysis of heated gas made with paraffin absorption and explosion.

Temperature of gas in tube	800° C.	900° C.	1000° C.	1200° C.
Unsaturated hydrocarbons	91·90	84·31	45·31	18·31
Saturated hydrocarbons—				
By paraffin	1·63 ⎱ 2·23	5·00 ⎱ 6·48	6·71 ⎱ 30·11	4·56 ⎱ 28·57
By explosion	0·60 ⎰	1·48 ⎰	23·40 ⎰	24·01 ⎰
Hydrogen	3·26	4·67	19·65	49·51
Carbon monoxide	1·11	1·40	1·23	1·10
Carbon dioxide	nil	nil	nil	nil

II. Analysis of heated gas made without paraffin absorption.

Unsaturated hydrocarbons	92·0	84·15	45·72	18·20
Methane calculated from CO_2	4·1	10·25	34·11	28·79
Carbon monoxide	1·2	1·50	1·28	1·0

III. Carbon dioxide from total explosion.

Calculated from Analysis II	189·3	180·7	129·2	69·31
Found	190·0	182·4	133·4	69·00
Carbon deposited in tube, grams per 100 c.c. of gas	trace	trace	0·0101	0·2150
Oil formed per 100 c.c.	0·012		0·0573	0·0035
Vol. of gas before heating	521·7	lost	514	350
Vol. of gas after heating	469·1		460	470

These experiments show conclusively that when only flowing slowly through the tube a higher member of the paraffin group, probably ethane, is formed up to 900° C., whilst at 1000° C. the quantity has

rapidly diminished, and at 1200° C. methane is the only member of the series present.

In the same way a small trace of some unsaturated hydrocarbon, probably benzene, is present at the lower temperatures, but disappears when 1200° C. is reached.

The next step was to see if the action of heat upon ethane under the same conditions as those existing in the previous set of experiments bore out the results arrived at.

Ethane was prepared by acting on ethyl iodide with a copper-zinc couple in presence of water, and passing the evolved gas through fuming sulphuric acid to purify it.

Table III.—The Action of Heat upon flowing Ethane.

Percentage of ethane in original gas .	96·38	96·38	96·38	96·38
Temperature of gas in the decomposing tube	900° C.	1000° C.	1200° C.	1500° C.
Analysis of the gas after heating—				
Unsaturated hydrocarbons........	31·00	28·42	11·58	1·69
Containing acetylene	trace	0·30	1·80	0·91
Saturated hydrocarbons—Paraffin .	12·82	8·34	3·88	0·00
Methane.	12·01	12·73	21·86	20·62
Hydrogen........·..............	40·64	46·78	57·45	73·35
Carbon deposited and oil formed in grams per 100 c.c. of gas—				
Carbon	0·0	0·0	0·0126	0·0314
Oil........................	0·0	trace	trace	0·0

These results show that, even below 900° C., ethane decomposes with liberation of hydrogen and formation of unsaturated hydrocarbons, which on examination prove to consist of ethylene with small quantities of acetylene, rise of temperature completing this decomposition, and also causing the ethylene to decompose as before.

It is evident that, if ethane had been a primary product in the decomposition of ethylene, it would in turn have decomposed with liberation of hydrogen at or below 900° C., and hydrogen would have been found at that temperature as a product of the decomposition of the ethylene instead of its appearance being coincident with the deposition of carbon at 1200° C.

The fact that with a rapid flow I was unable to detect a trace of free hydrogen until carbon has begun to deposit, or *vice versâ*, shows the fallacy of the text-book equation

$$C_2H_4 = CH_4 + C,$$
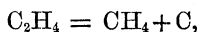
and on examining the evidence upon which the statement is based we find that Marchand,* who originated it, passed ethylene through glass and earthenware tubes heated to redness, and analysed the resulting

* ‘Journal für prakt. Chemie,’ vol. 26, p. 478.

products by passing them over heated copper oxide, and estimating the carbon dioxide and water vapour formed. At first the proportion of carbon to hydrogen was 100 to 17·236, which corresponds to nearly pure ethylene, and on heating to a higher temperature the ratio altered to 100 carbon to 30·771 hydrogen, which nearly corresponds to methane, carbon being at the same time deposited ; but this is manifestly no proof of the gas being methane, as a mixture of undecomposed ethylene and hydrogen, or mixtures of ethylene, methane, and hydrogen, such as those formed at 1200° C., would give the same result.

His results were to a certain extent confirmed by Buff and Hofmann, who noticed that when the platinum spiral was heated in pure ethylene there was at once a deposition of carbon, whilst the gas scarcely expands, from which they concluded that methane had been formed at the same time. When, however, the experiments tabulated in Table I are examined, it will be seen that as soon as 1200° C. is reached and carbon is deposited expansion takes place ; but that at all temperatures short of that there is contraction due to some of the gaseous products undergoing polymerisation and yielding liquids.   In Buff and Hofmann's experiment the gas in contact with the incandescent wire was decomposed with liberation of hydrogen and separation of carbon ; but the expansion caused by this action happened to be nearly equalised by the contraction due to polymerisation in the less heated portions of the gas.

The simultaneous appearance of carbon and hydrogen indicates clearly the liberation being due to the splitting up of a hydrocarbon, and the proportion in which these elements are liberated point to acetylene as being the body concerned.

In a paper read before the Chemical Society* I showed that in the interior of a luminous flame the olefines are to a great extent converted into acetylene, which decomposes at about 1200° C. with liberation of carbon, which, being heated partly by its own combustion and partly by the combustion of methane and hydrogen, becomes incandescent, and gives luminosity to the flame, and in the experiments which I have described I fully expected to find a higher percentage of acetylene; but the great tendency towards polymerisation which that body exhibits seems to at once determine its conversion into benzene, which can readily be distinguished among the liquid products, whilst a number of other more complex hydrocarbons are produced, among which crystals of naphthalene are conspicuous.

In order to ascertain if the behaviour of acetylene when passed through the heated tube under the conditions of these experiments gave results which support this view, acetylene was prepared by the action of dilute hydrochloric acid on acetylide of copper.

* 'Chem. Soc. Jour.,' vol. 61, p. 322.

Analysis of Original Gas.

Acetylene...................... 94·28
Oxygen .... 1·12
Nitrogen...................... 4·60

The gas was passed through the platinum tube, 25 mm. of which was heated to a temperature of 1000° C.

Analysis of the Heated Gas.

Acetylene	25·95
Other unsaturated hydrocarbons .	61·97
Saturated hydrocarbons	3·21
Carbon monoxide	1·01
Oxygen	0·38
Hydrogen....................	1·50
Nitrogen.....	5·98
	100·00

Carbon and Oil formed per 100 c.c. of gas.

Oil .... 0·095
Carbon .... 0·018

Volume before heating.... 309 c.c.
„ after „ .... 174·2 c.c.

showing that even under these conditions nearly three quarters of the acetylene had undergone polymerisation, so that it is probable that in the case of nascent acetylene, liberated from ethylene by the action of heat, the condensation of the acetylene molecules to form benzene would be practically instantaneous, unless the temperature were sufficiently high to cause dissociation to carbon and hydrogen at the moment of liberation.

The unsaturated hydrocarbons consisted chiefly of ethylene with some benzene vapour, the ethylene probably having been formed by the direct combination of acetylene and hydrogen, an interaction first noticed by Berthelot,

$$C_2H_2 + H_2 = C_2H_4.$$
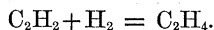
This also accounts for the small quantity of free hydrogen found on analysis, which, having regard to the amount of carbon deposited, should have been considerably higher.

It will be noticed that with the rate of flow employed in the experiments shown in Table I, the largest amount of acetylene found in the gas after heating was 3·60, which occurs just at the temperature when carbon begins to deposit freely, and is therefore sufficiently

high to check the polymerisation of the acetylene, and many attempts were made to find conditions under which the acetylene could be liberated and prevented from polymerising, and it was found that this could apparently be, to a certain extent, effected either by diluting the ethylene with a considerable volume of an inert gas, or else increasing the rate of flow through the heated tube.

On passing a mixture of 75 per cent. hydrogen and 25 per cent. ethylene through the tube, heated as before, 3·43 per cent. of acetylene was produced, which would be equivalent to 13·72 on the ethylene present, whilst the following results show the effect of increasing the rate of flow of the gas through the tube. The original gas taken was a bad sample containing 87·49 per cent. of ethylene and 12·51 of nitrogen, and the rate of flow was increased to 15 c.c. per minute, the tube being heated to 1250° C.

Unsaturated hydrocarbons.	10·41
„ „ containing acetylene .	4·49
Saturated hydrocarbons.	34·00
Hydrogen................................	41·99
Nitrogen................................	9·11
	100·00

Increase in volume .... Large
Carbon and oil deposited. ... 0·006 gram per 100 c.c.

showing a very marked increase in the amount of acetylene formed.

Before it was possible to trace the primary action taking place during the heating of ethylene, it was necessary to find how the temperatures and methods I was employing affected pure methane, which plays so important a part amongst the products of decomposition.

Methane was prepared by acting on methyl iodide by means of the copper zinc couple in the presence of alcohol and water.

Table IV.—The action of Heat upon flowing Methane.

Percentage of methane in the original gas	99·2	99·2	99·2	99·2
Temperature of gas in the decomposing tube	1000° C.	1200° C.	1300° C.	1500° C.
Analysis of gas after heating—				
Unsaturated hydrocarbons	trace	0·07	0·39	1·20
Containing acetylene	trace	0·07	0·39	0·963
Saturated hydrocarbons..........	97·65	90·00	88·52	19·22
Hydrogen......................	1·55	8·53	10·37	78·66
Carbon deposited and oil formed in grams per 100 c.c. of gas—				
Carbon	0·0	0·0	trace	0·015
Oil...........................	0·0023	0·0025	0·0005	0·0

These results show how much more stable methane is under the influence of heat than any of the other gaseous hydrocarbons studied.

It probably decomposes at first into acetylene and hydrogen, according to the equation

$$2CH_4 = C_2H_2 + 3H_2,$$
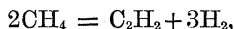
and then the acetylene either polymerises or decomposes to carbon and hydrogen, according to the temperature.

These results also explain why it is that the flame of methane when burning at an open tube is practically non-luminous, as, under these conditions, the maximum temperature of the flame is below 1100° C., and no formation of acetylene takes place; whilst with increase of temperature the flame becomes rapidly more and more luminous, so that when burnt in a regenerative burner at 1500° C. the light emitted is of considerable illuminating value.

As a further step in securing factors by which to trace the decomposition, it seemed advisable to attempt to trace the action of heat upon the benzene vapour formed by the polymerisation of the acetylene; and in order to do this, pure hydrogen was allowed to pass through benzene at a known rate and a constant temperature, the amount of benzene in the gas being determined.

Table V.—The Action of Heat upon Hydrogen-borne Benzene.

Percentage of benzene in original gas	5·28	5·28	5·28
Temperature of gas in the decomposing tube	900° C.	1100° C.	1300° C.
Analysis of the gas after heating.			
Unsaturated hydrocarbons	5·00	3·33	2·43
Containing acetylene	0·00	trace	0·083
Saturated hydrocarbons.................	0·00	2·87	5·02
Hydrogen.............................	95·00	93·80	92·47
Carbon deposited and oil formed in grams per 100 c.c. of gas.			
Carbon	0·0	trace	0·01
Oil.......	trace	0·012	0·00

which shows that the diluted benzene breaks down to acetylene, methane, and carbon, and, finally to carbon and hydrogen.

Taking the experimental data, it seemed to show that the primary reaction on heating ethylene is the splitting up of 3 mols. into acetylene and methane,

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$
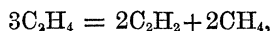
and that the acetylene then polymerises into higher bodies as

$$3C_2H_2 = C_6H_6,$$
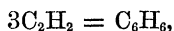
and that these compounds, by further polymerisation and interactions amongst themselves, of the kind studied by Berthelot and Carnelley,* give rise to a large number of others. As the temperature rises, the methane formed in the primary action splits up into acetylene and hydrogen,

$$2CH_4 = C_2H_2 + 3H_2;$$
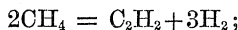
and when the temperature has reached the decomposing point of the acetylene, which varies with the degree of dilution, polymerisation takes place no longer, but the acetylene splits up directly into carbon and hydrogen, and all the products formed at lower temperatures doing the same thing, the final reaction is

$$C_2H_4 = C_2 + 2H_2.$$
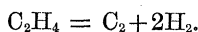
An attempt was now made to see how far analytical results would quantitatively bear out the inferences deduced from the foregoing experiments.

To do this, the method adopted was as follows:—The whole apparatus was filled with ethylene. The platinum tube and condensing tube were weighed, and the amount of ethylene in the gas holder measured. The platinum tube was heated to the required temperature, and the gas aspirated through it at a uniform rate of 4·2 c.c. per minute. When sufficient gas had passed through (about 250 c.c.) the stopcocks were turned off, and the amount of gas left in the holder measured. The amount of water displaced from the aspirator was also measured, and in this manner the change in volume was determined. The tube was again weighed, and the gain in weight noted. The platinum tube was also weighed, and then slowly heated to dull redness in a stream of hydrogen, in order to drive off any oil that might have been condensed in it, and again weighed. The tube was now heated to bright redness in a stream of oxygen, in order to burn off carbon, and again weighed. The sample tube was closed, and the contents analysed; the acetylene in the absorption bottles was also determined in the usual way.

Ethylene was first heated to 700—800° C., but no acetylene was formed, no alteration in volume took place, and the gas seemed unacted upon.

The temperature was then raised to 800—900° C., and the following results obtained.

Oil ....   0·0131 gram per 100 c.c. gas.
Heavy oil ....   0·0055   ,,   ,,
Carbon ....   Nil
Decrease in volume   100 to 89
Acetylene formed .   0·057 per cent.

* 'Chem. Soc. Journ.,' vol. 37, p. 701.

On analysis the gas gave—

1. Acetylene	0·06
Unsaturated hydrocarbons	81·38
Paraffins	6·66 ⎱ 15·83
Marsh gas	9·17 ⎰
Hydrogen.....................	0·00
Nitrogen.....................	3·10
	100·37

Original gas—

Ethylene.....................	98·03
Nitrogen.....................	1·97
	100·00

Analysis without paraffin absorption—

2. Acetylene.....................	0·06
Unsaturated hydrocarbons	81·25
Saturated hydrocarbons	17·70
Hydrogen.....................	0·00
Nitrogen.....................	3·10
	102·11

0·0186 gram of oil = 17·3 c.c. of acetylene at 17° C. and 760 mm. 100 vols. of gas after heating condense to 89 vols. gas and 15·4 vols. acetylene.

Calculating the analysis from a percentage to a basis of 89, we get—

Acetylene.....................	0·05
Unsaturated hydrocarbons	72·41
Saturated hydrocarbons	14·00
Hydrogen	0·00
Nitrogen.....................	2·76
	89·22

Taking 72·41 from 98·03 = 25·62 of ethylene decomposed, and, according to the equation $3C_2H_4 = 2C_2H_2 + 2CH_4$, 25·62 should give—

Calculated   17 vols. of acetylene and 17 vols. of methane
Found. ...   15·4   „   „   14   „   „

the discrepancy in the figures being due to interactions between the products of decomposition, and the result would certainly seem to point to the above equation as representing the initial decomposition.

The next temperature tried was 900—1000° C., and the following figures were obtained :—

Rate of flow........   4·2 c.c. of gas per minute.
Oil...............   0·0213 gram per 100 c.c. gas.
Heavy oil ....   0·0080   „   „
Carbon ....   0·0363   „   „
Decrease in volume..   100 to 98·6

On analysis the gas gave—
    1. Acetylene........................   1·19
       Unsaturated hydrocarbons ......   15·21
       Paraffins........................   12·70 ⎫
       Methane......................   27·78 ⎬ 40·48
       Hydrogen......................   41·30
       Nitrogen......................   1·82
                      —————
                      100·00

No paraffin absorption—
    2. Acetylene ....   1·19
       Unsaturated hydrocarbons ......   15·43
       Saturated hydrocarbons.........   40·77
       Hydrogen ....   40·79
       Nitrogen......................   1·82
                      —————
                      100·00

Explosion of the whole—
    Carbon dioxide................   73·73 per cent.
      „   „   calculated from 1   73·28   „
      „   „   „   „   2   73·96   „

0·0363 gram of carbon = 36·3 c.c. of acetylene at 19° C. and 762 mm.

0·0293 gram of oil = 27·0 c.c. of acetylene at 19° C. and 762 mm.

Calculating these from 100 c.c. of gas to 98·6 c.c. of gas, we get—

    Oil   = 26·8 c.c. of acetylene at 19° C.
   Carbon = 35·8 c.c.   „   „

And calculating the gas analysis in the same manner as before, we obtain:—

       Acetylene ....   1·17
       Unsaturated hydrocarbons ......   15·00
       Saturated hydrocarbons ....   39·90
       Hydrogen.....................   40·72
       Nitrogen ....   1·81
                     —————
                     98·60

Then the amount of ethylene decomposed is $98\cdot03-15\cdot00 = 83\cdot03$, and this should give

$$3C_2H_4 = 2C_2H_2 + 2CH_4.$$

| 83·03	55·35	55·35 calculated.
	62·6	39·9 found.
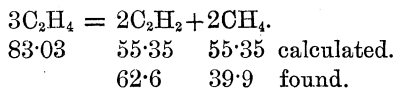
Evidently, therefore, some of the methane has decomposed, forming acetylene and hydrogen. Amount of methane decomposed $55\cdot35-39\cdot9 = 15\cdot45$,

$$2CH_4 = C_2H_2 + 3H_2.$$

15·45   7·72   23·16
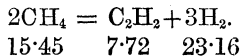
Adding this acetylene on to that already calculated for the decomposition of ethylene, we get $55\cdot35 + 7\cdot72 = 63\cdot07$, a figure nearly equal to the acetylene found.

Taking into consideration the complexity of the changes involved and the difficulty in obtaining great accuracy in gas analysis, these results seem to me to prove that the primary action of heat upon ethylene may be represented by the equation

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$
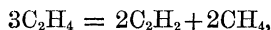
whilst the final decomposition is as represented by previous observers,

$$C_2H_4 = C_2 + 2H_2,$$
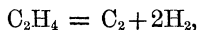
and that between these two extremes there occur a large number of interactions due to the polymerisation of the acetylene formed from the ethylene, and also at higher temperatures from the methane, according to the equation

$$2CH_4 = C_2H_2 + 3H_2.$$
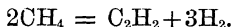
In conclusion, I desire to acknowledge my indebtedness to Mr. F. B. Grundy for the assistance he has rendered me in this investigation.